Describe — Top-down and bottom-up technique of nanomaterials synthesis.

→

Top-down:— When a bulk material is machined & modified for desired structure then it's called top-down technique.

Example, Lithography, Ball milling, manufacturing of IC.

merits:— (i) Deposition over a large substance is possible, so large scale production is possible.
(ii) chemical purification is not required.
(iii) It's very suitable for laboratory experimentation.

De-merits:— (i) It yields broad size distribution (10-100)nm.
(ii) It creates various particles shape and geometry.
(iii) Impurities such as stress defects, imperfections get introduced.
(iv) It's very expensive technique.

Bottom-up:— It's used to build something from basic materials like assembling materials from the atoms or molecular level to structure of comparatively higher size.

Example:— Sol-gel, PVD, CVD, Electro deposition, self assembly of nanomaterials.

marits:- (i) Accurate nanostructures can be obtained by this approach as it enables the realization of true nano ~~structure~~ scale. building Blocks that originate from the atomic scale.

(ii) Deposition parameters can be controlled.

(iii) Narrow size distribution is possible (1-20) nm

(iv) cheaper technique and less chance of contaminations of materials.

De-marits:- (i) It requires compatible surfaces.

(ii) It requires sufficient molecules, if not possible, the process cannot be possible. so, large scale production is difficult.

(iii) Stress, defect and imperfactions gets introduced.

What do you mean by quantum confinement. What are the consequences of quantum confinement in different dimensional nanostructured materials.

What is a quantum Well. Give the schematic of wave functions of the first three confined states and energies of the first three confined states of an infinite depth potential.

p-710 (Lithography)
p-161 (Ball milling)

Two different approaches of material fabrication

1) Top down approach
2) Bottom-up approach.

Top-down approach

Generally a bulk material is taken and machined it to modify into the desired shape and product.

e.g → 1) Manufacturing of integrated circuits using a sequence of steps such as crystal growth, lithography, etching, ion implantation etc.

2) Ball milling → where macrocrystalline structures are broken down into nanocrystalline structures, but original integrity of the material is retained.

3) lithographic technique.

Bottom up approach →

It is used to build something from basic materials like assembly materials from the atoms/molecules up.

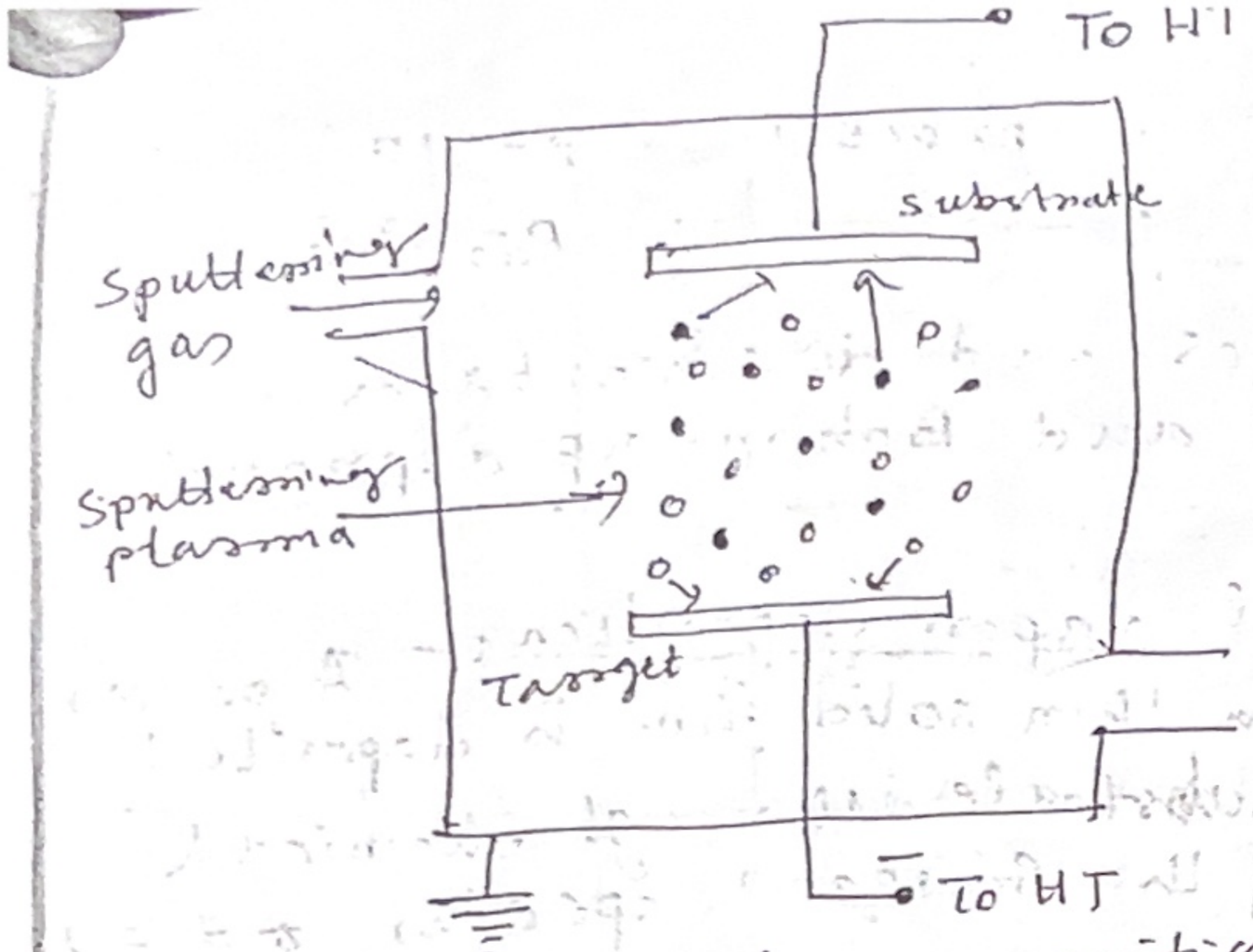
e.g → i) Self assembly of nanomaterials
ii) Sol-gel technology
iii) Electrodeposition
iv) physical and chemical vapour deposition (PVD, CVD),
v) Epitaxial growth
vi) Laser ablation.

p-110 → Lithography
p-161 → Ball milling

Lithographic process → p-110
Ball milling → p-161, Rao 136
Advantages and disadvantages of top-down and Bottom-up approach

Chemical vapor deposition :- A process where a thin solid film is deposited on to a substrate through chemical reactions of the gaseous species

p-113 Physical vapour deposition is a physical process where atoms in a solid target material are ejected into the gas phase due to bombardment of the material by energetic ions usually or commonly used for thin film deposition. The process is of driven by momentum exchange between the ions (non-reactive ions like Ar) and atoms in the material, due to collisions, (e.g → sputtering). A glow-discharge (plasma) of non-reactive ions (Ar) is created by a potential difference inside a vacuum chamber, which fall on the target (the material to be deposited) and break



* material composition
* Thickness of the film
* homogeneity of the film
* deposition rate
* deposition time
* Substrate temperature (to prevent agglomeration of the particles into bigger clusters) and to retain or remain in nano crystalline form

} can be easily controlled by this process

It provides produces film of high purity, greater adhesive strength, homogeneity and desired film thickness.

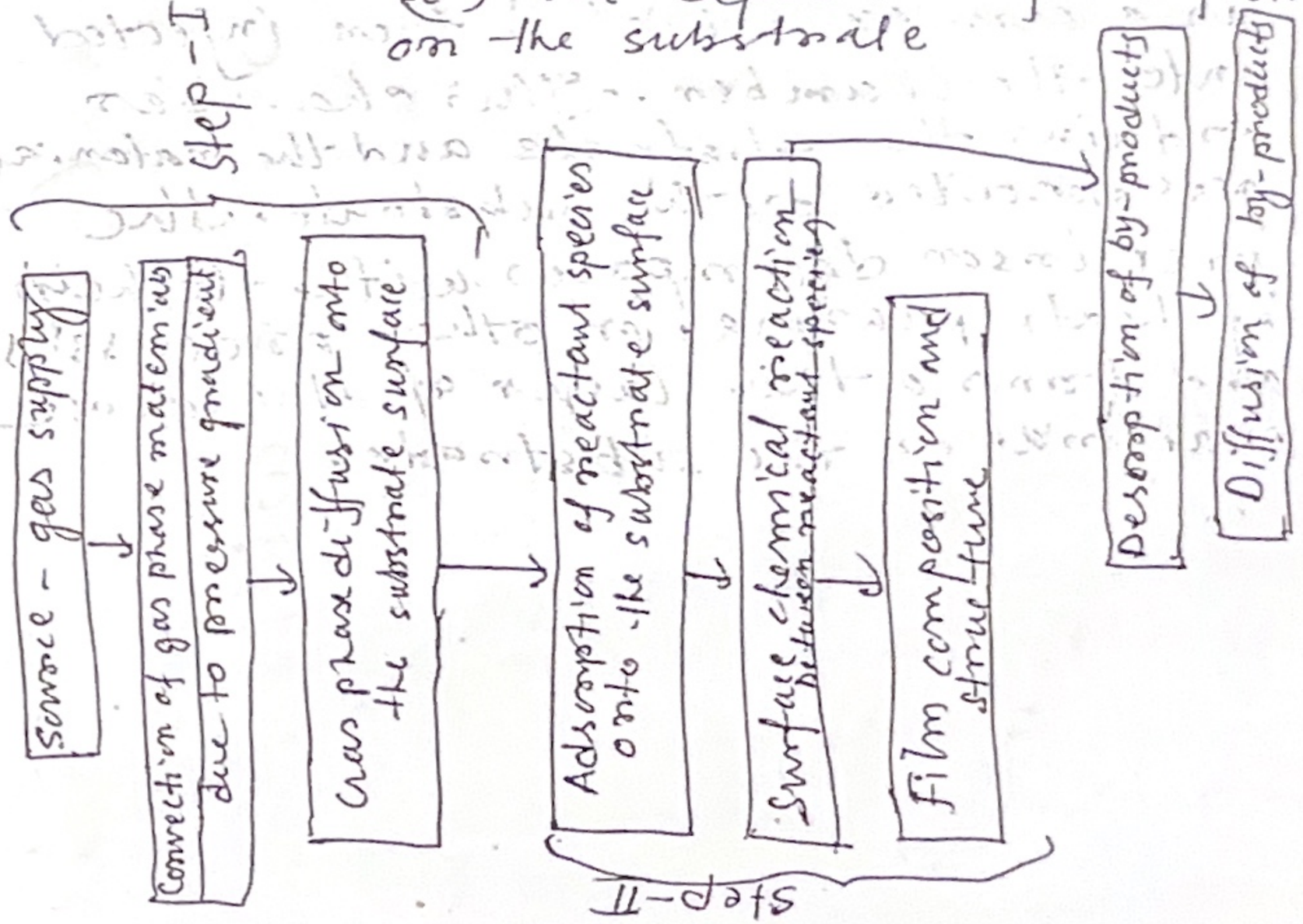
* loose cluster of atoms and then asse controlled on the surface to be coated. Initially this method was used to metal films, but later on compound material are also deposited in this method. In case target stoichiometry is a critical parameter to deposit compound material due to deposition mi...

p-121

CVD :- It is a technique for synthesizing materials in which chemical components in vapour phase react to form a solid film at some surface (substrate). In general, the CVD process can be devided into two Broad steps →

i) One is transport of gas phase materials to the reaction zone and the reaction of materials

ii) the deposition of the film on the substrate


Step-I
Source - gas supply
Convection of gas phase materials due to pressure gradient
Gas phase diffusion onto the substrate surface
Step-II
Adsorption of reactant species onto the substrate surface
Surface chemical reaction between reactant species
Film composition and structure
Desorption of by-products
Diffusion of by-products

Difference between PVD and CVD

PVD uses physical processes. In PVD a pure source material is first evaporated which then condenses on the substrate material eventually leading to the fabrication of a thin film of the material.

CVD mainly uses chemical process. Here the source material is mixed with a volatile precursor that acts as a carriers which is then injected into the chamber. This chamber contains the substrate and the material gets deposited on this substrate. The precursor decomposes with the help of heat, plasma, or other processes and forms a thin layer of the source material on the substrate.

~~Different~~

Short note on — ~~or PVD~~

1) Thermal evaporation
2) E-beam evaporation
3) Pulsed Laser deposition.

Short note on — ~~or ESD~~

1) Sol-gel
2) Electro deposition.
3) Hydrothermal growth (or synthesis)

sol-gel → Wet-chemical based self-assembly process for nanomaterial formation

~~#~~ Sol is a homogeneous dispersion of soluble solids and miscible liquids consisting of finely divided and discrete particles of 1-10 nm in diameter. e.g- Milk of magnesia, paints.

~~#~~ Gels are colloids ~~x~~ or semisolids in which the liquid medium has become viscous enough to behave more or less as a solid. It is jelly like. ~~or~~ and notably elastic.

In sol-gel process, the gelation of sol is converted (form) into a network structure of continuous liquid phase, called gel. Generally sol-gel formation occurs in few steps: —

1) The evolution of networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel)
   1) Hydrolysis and alcoholysis
   2) Water and alcohol condensation and polymerization of monomers to form particles
   3) growth of particles
   4) Agglomeration of particles followed by the formation of networks throughout the liquid medium resulting in thick gel.

The whole process depends on following conditions: — 1) pH value of the sol,
2) temp. of the reaction,
3) reagent concentrations
4) time of reaction,
5) nature and concentration of catalyst

6) H_2O/cation ratio
7) ageing temperature
8) time of the gel-formation

Once the gel is formed, there are several ways to convert this gel (inorganic network) to the desired solid form. Depending on the deposition and drying processes or conditions, this gel can be converted into various forms such as aerogel, xerogel, gelled spheres, nano-powders, thin film coatings, nanostructured layers etc. which is shown in figure 9.

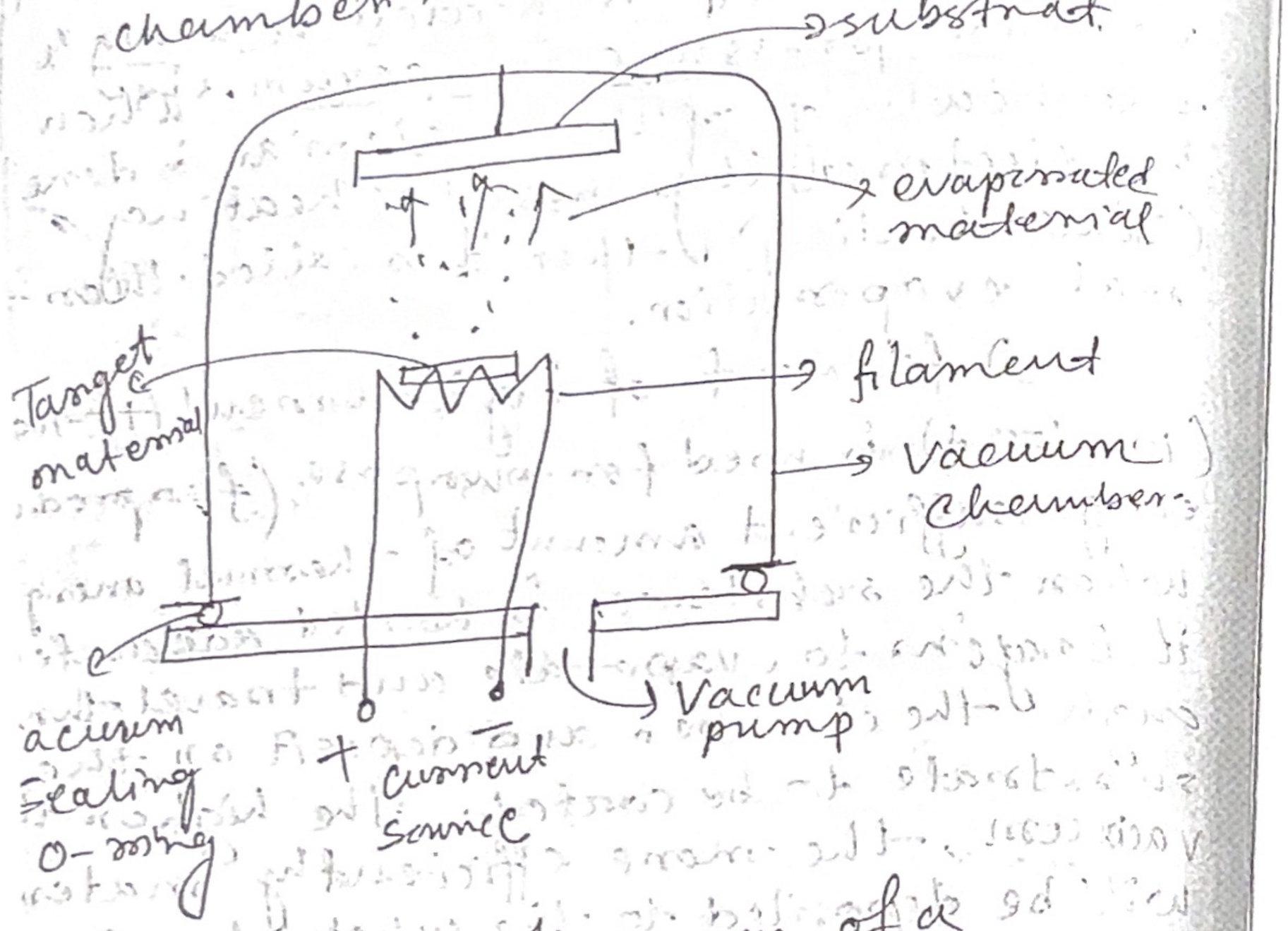
P-143

Thermal evaporation:-

Evaporative depositions of thin films is a process where the material to be deposited is heated to a high vapour pressure in vacuum. When the heating of the material is done by electrically resistive heating (Joule heating) then it is called thermal evaporation.

A filament of high current (10-100 A) is used for purpose (for producing sufficient amount of thermal energy) when the substance is heated adequately it begins to evaporate and travel through the chamber and deposit on the substrate to be coated. The higher the vacuum, the more efficiently material will be deposited to the substrate. Because in higher vacuum, there are less no. of molecules in the chamber which will increase mean free path and a longer mean free path will allow the evaporated molecules to travel further before striking an unwanted molecule

so the rate of deposition depends upon the current being passed through the filament and also on vapour pressure inside the chamber.



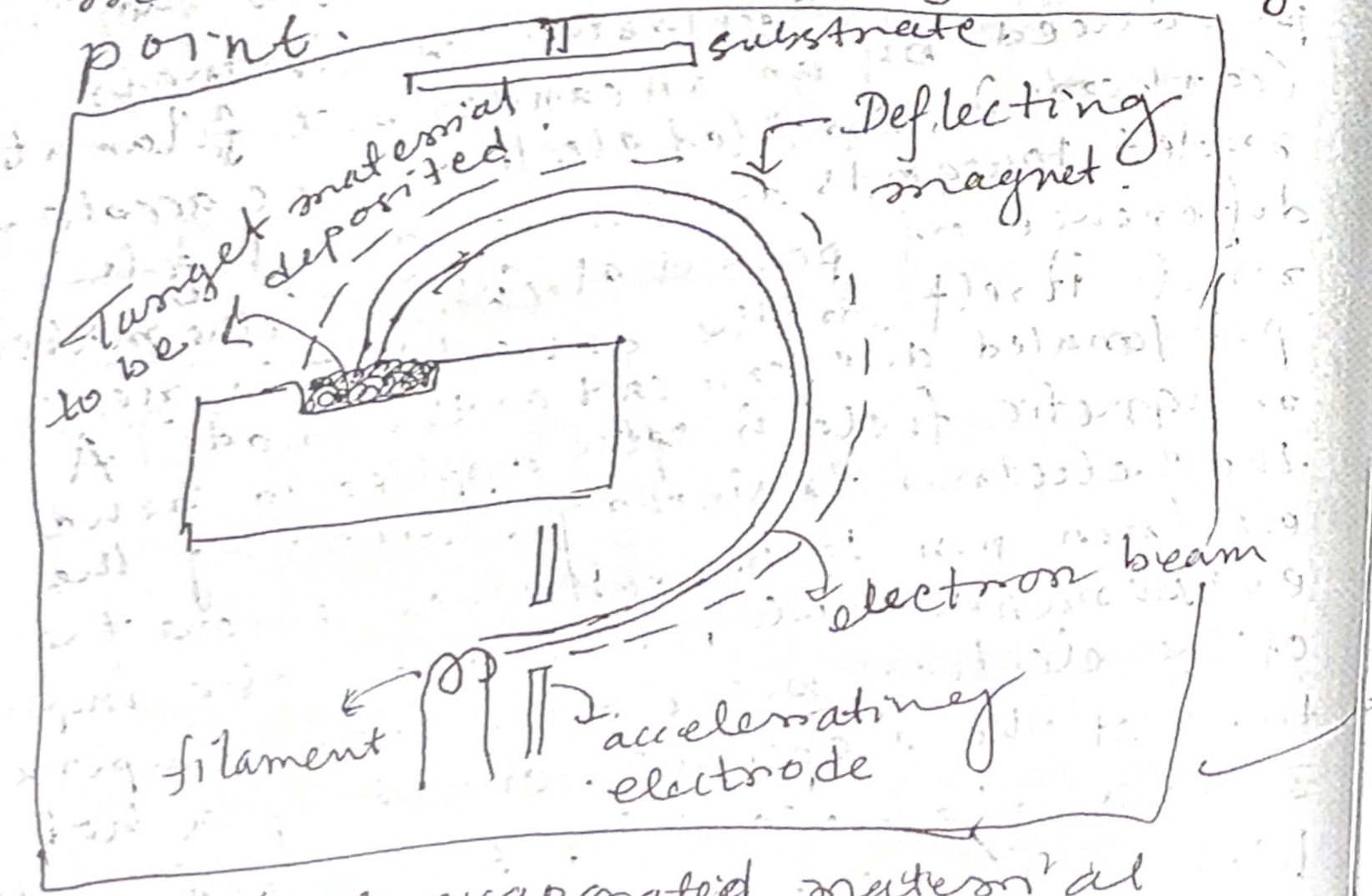
Schematic diagram of a thermal evaporation system

e-beam evaporation:-

When the heating of the material to be deposited or the substrate in evaporative deposition method is done by high energy electron beam bombardment, it is called e-beam evaporation process.

The electron beam is generated by an electron gun, which uses the thermionic emission of electrons produced by an incandescent filament (cathode). Emitted electrons are accelerated towards an anode by a high difference of potential (kV). [The material itself or the crucible or a near perforated disc can act as the anode.] A magnetic field is often applied to bend the electron trajectory, allowing the electron gun to be positioned below the evaporation line. The energetic impact of the electron beam raises the temperature of the evaporant, creating a hot zone on the material. At a sufficiently high temp., the material will begin to

evaporate. As electrons can be localized, it is possible to obtain a much localised heating on the material to evaporate with a high density of evaporation power (several kW). This allows controlling the evaporation rate, from low to high value and chance of depositing materials with high melting point.



After that evaporated material is deposited on the substrate.

Pulsed Laser Deposition:-

Pulsed Laser Deposition (PLD) technique is used for thin film deposition as well as nano material synthesis. In this process, a high power pulsed laser beam is focused inside a vacuum chamber to strike a target of the desired material and composition to vaporise the target and deposit materials on a substrate.

The deposition generally takes place in ultra high vacuum or in the presence of some background gas of certain pressure. Some neutral gases such as Ar are used at some desired pressure to control the deposition rate as well the film composition whereas reactive gases like oxygen or nitrogen are sometimes used to deposit oxide or nitride materials. P.T.O

Electron beams are accelerated from a heated filament towards the source by accelerating anodes and magnetic field. Due to bombardment of highly energetic electron beam, local heat is generated at the source, which evaporates the material

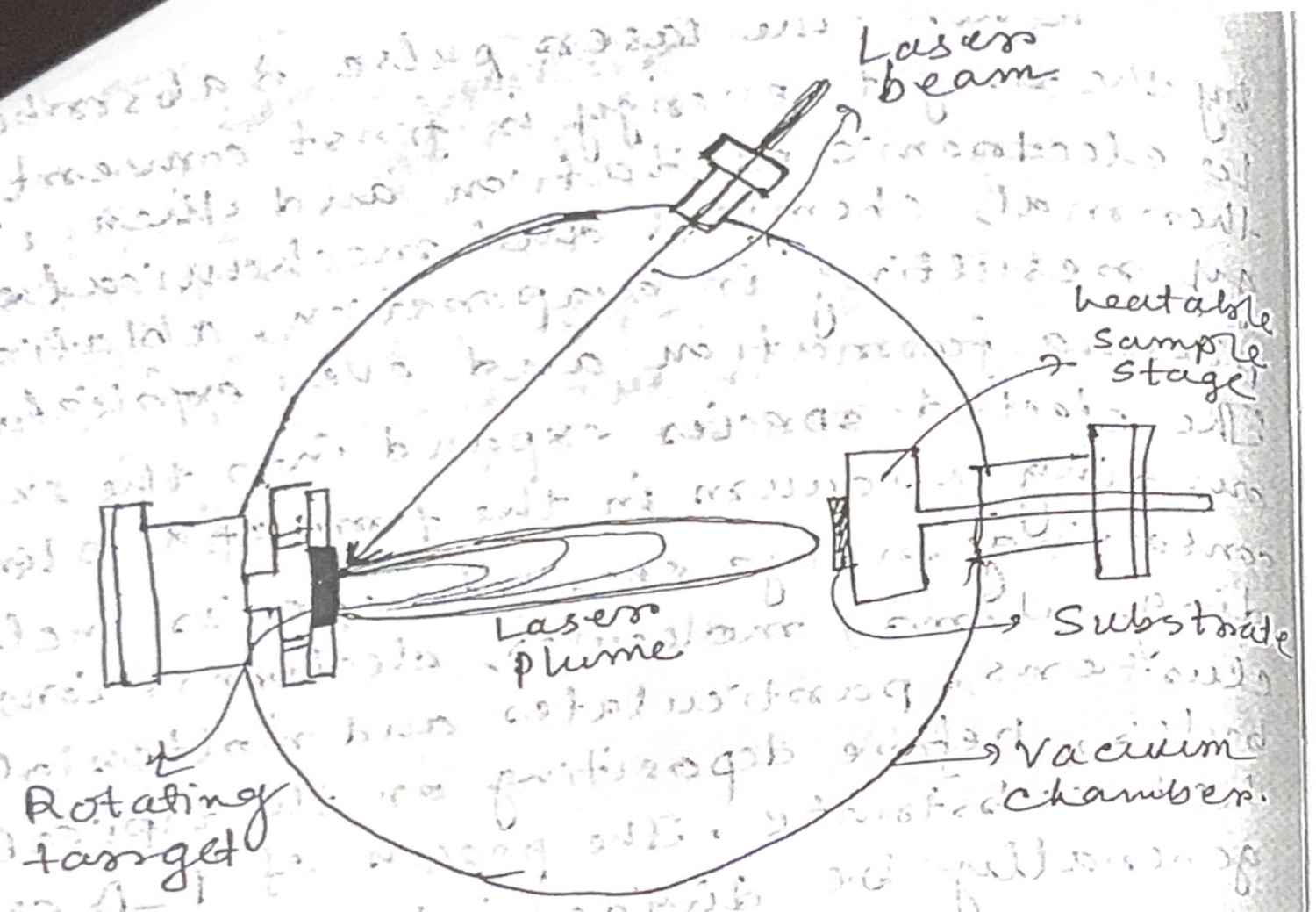
PLD is utilised to fabricate high quality crystalline films and also to deposite materials of complex stoichiometry e.g. superconducting $YBa_2Cu_3O_7$ thin film like multi-element oxides, nitrides, metallic multilayers and various superlattices.

The physical pheonomena of laser-target interaction and film growth are quite complex. The target material which is evaporated by the laser is normally found as a rotating disc attached to a support. It can be sintered into a cylindrical rod with rotational motion and a translational up and down movement along its axis involves.

PLD relies on a photon interaction to create an ejected plume of material from any target. The vapour (plume) is collected on a substrate placed a short distance from the target.

When the laser pulse is absorbed by the target, energy is first converted to electronic excitation and then into thermal, chemical and mechanical energy resulting in evaporation, ablation, plasma formation and even exfoliation. The ejected species expand into the surrounding vacuum in the form of a plume containing many energetic species including atoms, molecules, electrons, ions, clusters, particulates and molten globules, before depositing on the typically hot substrate. The proces of PLD can generally be divided into four stages

i) Laser ablation of the target material and creation of a plasm
ii) Dynamics of the plasma
iii) Deposition of the ablation material on the substrate
iv) Nucleation and growth of the film on the substrate surface.



Basic Step up of PLD System:-

* Laser beam is collimated through lenses to the target for ablation.
* Target can be rotated
* A laser plume is generated between target and the substrate
* The substrate can be rotated as well as heated (if needed) for uniform film deposition.

p-155

Electrodeposition:- Electrodeposition is a liquid-based deposition process where an electrical current is passed through a polar liquid by applying an electric potential between two electrodes. Then the liquid breaks into ions and other charged compounds and depending on the charge on the ions/compounds and the potential of the electrodes, these charged materials deposit on the electrodes. By suitable arrangements of preferred substrates on the electrodes, one can coat thin layers of films of some desired materials on the substrate. A schematic diagram of the electrodeposition apparatus is as shown in fig.

fig is on next page

Electrodeposition offers rigid control of film-thickness, uniformity, deposition rate, low equipment cost and starting materials. Due to the use of an electric field, electrodeposition is particularly

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suited for the formation of uniform films on substrates of complicated shapes, impregnation of porous substrates and deposition on selected areas of the substrate.

e.g:- Electroplating, Electrophoretic deposition of ceramic films (EPD), electrolytic deposition (ELD)

are the manufacturing of integrated circuits using a sequence of steps such as crystal growth, lithography, etching, ion implantation, etc. For nanomaterial synthesis, ball-milling is an important top-down approach, where macrocrystalline structures are broken down to nanocrystalline structures, but original integrity of the material is retained. Sometimes this method is used to prepare nanostructured metal oxides by chemical reaction between two constituents during crushing. The crystallites are allowed to react with each other by the supply of kinetic energy during milling process to form the required nanostructured oxide.

On the other hand, bottom-up technique is used to build something from basic materials, for example, assembling materials from the atoms/molecules up, and, therefore very important for nano-fabrication. Unlike lithographic technique of top-down approach, which is extensively used in silicon industry, this bottom-up nonlithographic approach of nanomaterial synthesis is not completely proven in manufacturing yet, but has great potential to become important alternative to lithographic process. Examples of bottom-up technique are self-assembly of nanomaterials, sol–gel technology, electrodeposition, physical and chemical vapour deposition (PVD, CVD), epitaxial growth, laser ablation, etc. Details of these procedures are discussed in the subsequent sections.

6.3 LITHOGRAPHIC PROCESS AND ITS LIMITATIONS

A great deal of brilliant science and engineering involving mesoscopic structures was made possible over the past decade through the use of advanced lithographic technologies [15–16]. Lithography is a printing method that uses chemical processes to create an image. There are two types of lithographic processes used in silicon industry; one is called photolithography and the other as electron-beam (e-beam) lithography. Photolithographic process uses light to transfer a geometric pattern from a photomask to a light-sensitive chemical (photoresist) on the substrate (as shown in Fig. 6.1). Depending on the pattern on the photomask, various structures can be generated on the substrate, which is further used to develop different silicon-based photonic and electronic devices. Current state-of-the-art photolithography tools use deep ultraviolet (DUV) light with wavelengths of 248 and 193 nm, which allow minimum feature sizes down to 50 nm.

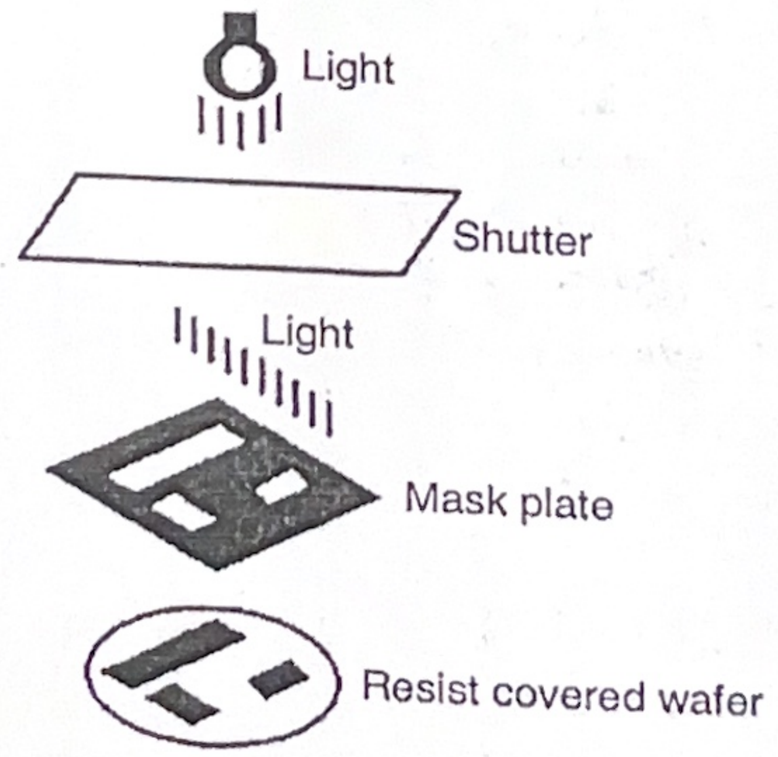

Fig. 6.1 Schematic diagram of lithographic fabrication technique.

On the other hand, electron beam lithography is the process of using a beam of electrons to generate patterns on a surface (cf. Fig. 6.2). Primary advantage of this technique is that it is one of the ways to beat the diffraction limit of light and make features in the sub-micrometer regime. Due to very slow speed, this form of lithography has yet to become a standard technique in industry but found wide usage in research, although this form of lithography has found wide usage in mask-making (for masks used in photolithography) and low-volume production of semiconductor components. Such systems have produced linewidths of ~20 nm. But these techniques seem to be approaching their limits for fabricating one-dimensional (1D) and 0D nanostructures of very small size. Therefore, alternative nonlithographic approaches to nanostructure fabrication are the need of the hour.

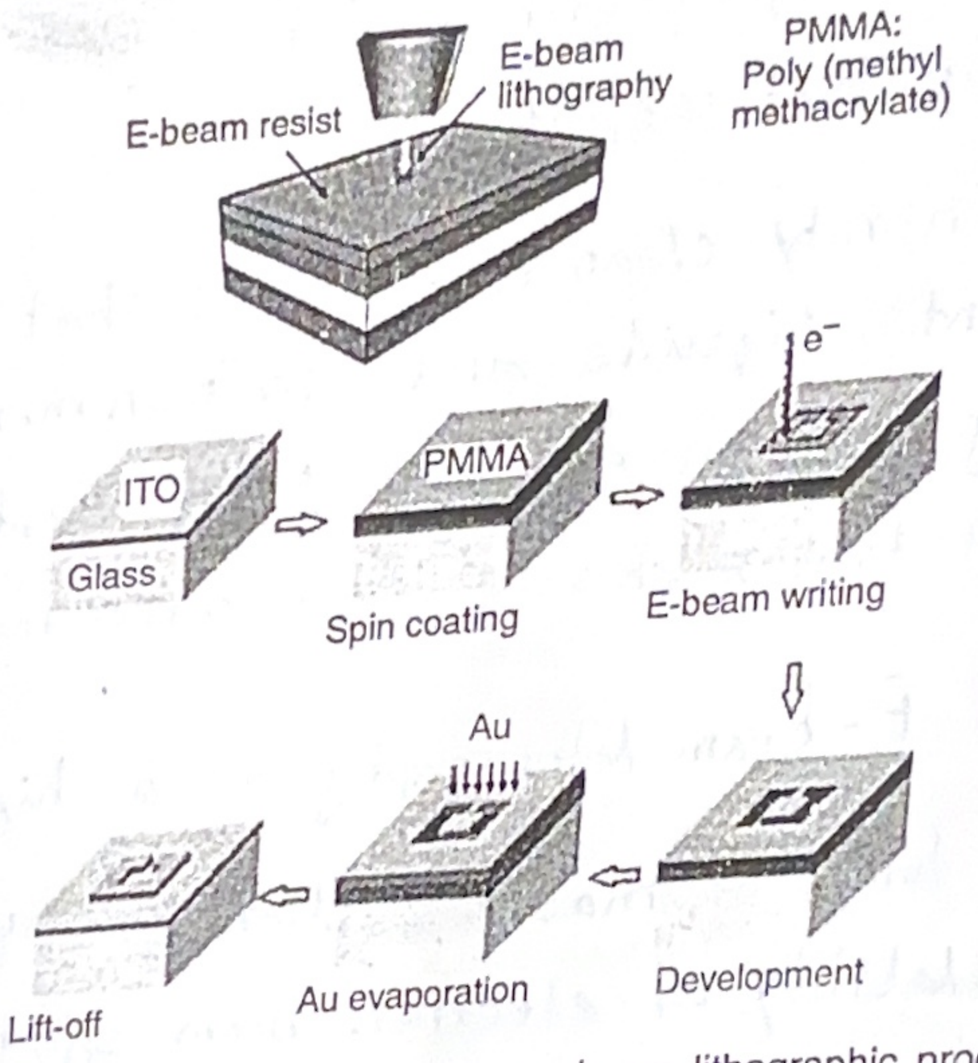

Fig. 6.2 Schematic diagram of electron-beam lithographic process.

6.4 NONLITHOGRAPHIC TECHNIQUES

Nonlithographic techniques are based on natural self-organization processes. In general, these techniques can be broadly divided into two groups: vacuum-based deposition process and solution-based deposition process. In vacuum-based syntheses, deposition takes place under high vacuum (~10^{-8} to 10^{-11} mbar). Therefore, the process is very clean; probability of deposition of foreign and undesired materials is very low. Hence these types of techniques are highly favourable for efficient device fabrication. But the vacuum-based systems require costly and complicated equipment, with leak-proof accessories, vacuum pumps, gauges, etc. Examples of these types of techniques are, evaporation, sputtering, chemical vapour deposition, laser ablation, molecular beam epitaxy, plasma arc method, etc.

Solution-based syntheses processes, on the other hand, are based on chemical reactions in liquid phase. Therefore, these techniques are simple and cost-effective and most importantly,

Advantages :-

(i) photolithography can create extremely small patterns.

(ii) photolithography exercises exact control over the shape and size of the objects it creates.

Disadvantage_

(i) It requires a completely flat substrate in order to produce effective patterns. It is not efficient at producing non-flat objects.

(ii) It requires extremly clean conditions that are void (free) of all contaminants, liquids and environmental hazards.

(iii) photolithography requirse ideal temp conditions.

(iv) Generation of the masks is time consuming and expensive.

Advantages :- (i) E-beam lithography has a high resolution.

(ii) Most common form of maskless lithography due to wide range of availability of electron beam systems with wide range of e-beam energies (10-100 keV)

(iii) Minimum feature size can be about 5 nm.

Disadvantages :- (i) E-beam can damage the substrate as there is no gap b/t substrate and resist.

(ii) The technique is slower than 'Photolith.. because of the use of serial ~~lig~~ lithographic system.